

Rapid Excited State Structural Reorganization Captured by Pulsed X-Rays

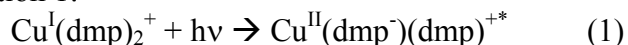
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Molecular excited states have important applications as luminescent probes and in solar energy conversion, photography, sensing, and displays. A wide variety of theoretical and experimental techniques have been employed to provide insights into the fascinating structures of excited states and the distortions that accompany excited state relaxation. Despite their importance, however, identification of the absolute molecular structure of excited states remains elusive. In collaboration with Dr. Lin Chen and her colleagues, we recently reported the first X-ray spectroscopic characterization (including x-ray absorption fine structure, XAFS, and x-ray absorption near edge structure, XANES) of a molecular excited state.¹ This important achievement was made possible with the aid of x-ray pulses from a new generation synchrotron source at Argonne National Laboratory with a significantly higher x-ray photon flux than was previously unavailable. Significantly, the x-ray characterization was accomplished in fluid solution at room temperature.

The metal-to-ligand charge transfer (MLCT) excited states of copper(I) diimine compounds were chosen as the first test study.² There exists compelling literature evidence for novel excited state structural reorganization in this class of compounds. These reorganization processes are relevant to “gated” electron transfer in proteins as well as in new classes of molecular devices and solar energy conversion materials. Therefore, these studies represented a proof-of-concept example of excited state characterization and also provide new insights into the dynamics for structural reorganization important in biology and chemistry.²

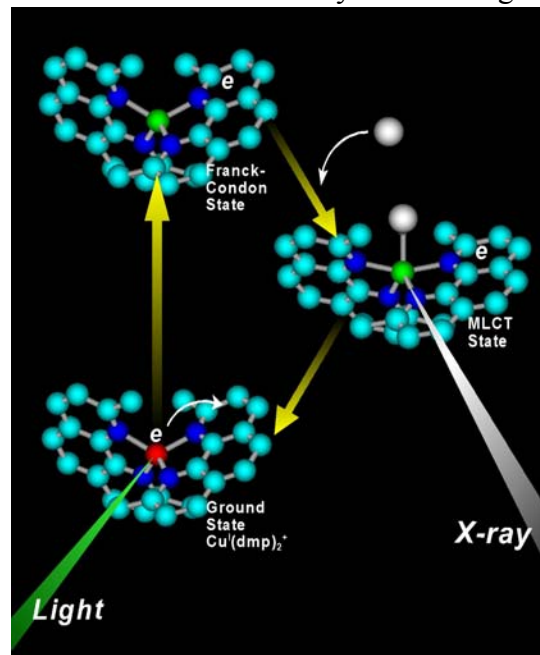
The origin of the photo-driven structural change can be understood by considering light absorption by a cuprous diimine compound, such as $\text{Cu}^{\text{I}}(\text{dmp})_2^+$, where dmp is 2,9-dimethyl-1,10-phenanthroline, Equation 1:



The Cu(I) ground state has a d^{10} electronic configuration with a tetrahedral geometry in fluid solution. Absorption of a visible photon promotes an electron from copper to a dmp ligand, MLCT, to form an excited state with a formally Cu(II) center coordinated to one reduced and one neutral dmp ligand. The Cu(II) center in the excited state has a d^9 electron configuration and is subject to a significant Jahn-Teller distortion. The observations of large “Stokes-like” shifts between the absorption and photoluminescence spectra and represent strong evidence that the excited state adopts a more Cu(II) like geometry. In addition, the excited state is quenched in the presence of Lewis bases that

can for excited state complexes, exciplexes, with copper. The Jahn-Teller distortion is clearly manifest in the crystal structures of Cu(II) bipyridine and phenanthroline compounds that reveal distorted square pyramidal or trigonal bi-pyramidal geometries with an additional ligand derived from solvent molecule or counterion.²

The general idea of the proposed experiment is shown schematically. Pulsed light excitation a Cu(I) diimine compound instantaneously creates a Franck-Condon state with a Cu(II) excited state in a Cu(I) geometry. With our instrument response time, this state rapidly undergoes vibrational relaxation and Jahn-Teller distortions to yield an emissive thermally equilibrated excited state that lives for about 100 ns. The purpose of our initial studies was to capture the structure of this MLCT state at its optimal concentration rather than to monitor the population decay. In particular, our initial work investigated how the thermally equilibrated MLCT state structure differed from the corresponding Cu(I) and Cu(II) compounds in the ground state. It was in fact found that the excited state had x-ray properties very similar to that of the Cu(II) compound. Our data supports previous studies that have inferred large structural changes in copper diimine excited states. They have also revealed previously unrecognized behavior on the dynamics of excited state structural reorganization.



In more recent work, we have examined the solvent dependence of the structural changes by x-ray and picosecond spectroscopies. We have specifically looked at Lewis basic solvents that are known to quench the copper excited states by an ‘exciplex’ mechanism.³ In related work, we have discovered dissociative copper MLCT excited states that photorelease carbon monoxide and subsequently bind dioxygen.^{4,5} The fundamental implications of these studies as well as practical applications will be discussed.

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